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Citation for published version:

Bal, N & Rein, G 2013, 'Relevant model complexity for non-charring polymer pyrolysis', *Fire Safety Journal*, vol. 61, pp. 36-44. <https://doi.org/10.1016/j.firesaf.2013.08.015>

Digital Object Identifier (DOI):

[10.1016/j.firesaf.2013.08.015](https://doi.org/10.1016/j.firesaf.2013.08.015)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Publisher's PDF, also known as Version of record

Published In:

Fire Safety Journal

Publisher Rights Statement:

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Relevant model complexity for non-charring polymer pyrolysis[☆]



Nicolas Bal^{a,b}, Guillermo Rein^{a,c,*}

^a School of Engineering, University of Edinburgh, UK

^b Centre d'Etudes et de Recherches de l'Industrie du Béton, France

^c Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, UK

ARTICLE INFO

Article history:

Received 13 March 2013

Received in revised form

9 July 2013

Accepted 4 August 2013

Available online 30 August 2013

Keywords:

Sensitivity

Modelling complexity

PMMA

Pyrolysis

ABSTRACT

The choice of the heat, mass and chemical mechanisms included in a pyrolysis model is often subjective, and detailed justifications of the inclusion or exclusion of the different mechanisms are infrequent. The implicit assumption that models with a higher number of mechanisms reproduce more accurately the reality has led to the recent growth of complexity in pyrolysis modelling seen in the literature. However, as we show in this work, the comparison of several conceptual models predicting the same experimental results does not support this assumption, but reveals the presence of unnecessary complexity and multiple sources of uncertainty. Using a novel approach corresponding to a mechanism sensitivity, the influence of the heat, mass and chemical mechanisms on the transient predictions of surface temperature and mass loss rate (non-flaming conditions) for PolyMethylMethAcrylate (PMMA) samples is investigated. While a small change in the chemical degradation mechanism has a large effect on the predictions of the mass loss rate, the surface temperature is not affected. The heat transfer mechanisms appear to have however a significant effect on both quantities of interest. This study demonstrates that the use of complex chemical mechanisms (e.g. multi-step reaction scheme or oxidative reaction) is not justified if the mechanisms of the heat transfer are kept simple. It is therefore recommended to use consistent levels of crudeness dictated by the heat transfer.

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1. Introduction

While the choice of a conceptual¹ model is a major step in the prediction of a phenomenon, its justification is often subjective, and detailed justifications of inclusion or exclusion of the different mechanisms are infrequent. Assumptions and simplifications decrease the complexity of a model and define somehow its limitations. The implicit hypothesis that models with a higher number of mechanisms reproduce more accurately the reality has led computational modelling in general and fire modelling in particular to undergo recently a large growth in complexity [2–4].

Chwif et al. [5] have listed some of the reasons for this growth in complexity. Among the non-technical reasons, they highlight the

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* Corresponding author at: Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, UK. Tel.: +44 20 7594 7036.

E-mail addresses: n.bal@ed.ac.uk (N. Bal), g.rein@imperial.ac.uk (G. Rein).

¹ Note the difference between a conceptual model and its programmed code version. According to the ISO standard 16730:2008 [1] a conceptual model is the “description of all the information, mathematical modelling data and mathematical equations that describe the physical system or process of interest”. It is called model hereafter for simplicity.

“include all” syndrome and the “possibility” factor. The former is the consequence of the inexperience of the modellers who might feel insecure and include the maximum number of mechanisms just in case. The latter is due to the increasing computational power available which makes possible to include a significantly higher number of mechanisms without increasing the running time. One example of the technical reasons listed is the willingness of gathering the needs of several users, thus increasing the scope of the model and the number of mechanisms.

However, as the global level of complexity increases in models, the number of input parameters required increases as well. These parameters could be, for example, physical properties (or effective properties), mathematical constants, experimental constants or calibration factors, and all carry some degree of uncertainty. Their respective uncertainty accumulates in the model and contributes to the global uncertainty associated with the numerical predictions. The discrepancy between the experiments and the predictions is a combination of errors due to the lack of important mechanisms (continuous line in Fig. 1) and the parameter uncertainty (dashed line in Fig. 1) [6,7].

An equilibrium is therefore required between the error related to the simplicity of the model equations and the prediction uncertainty in order to find an appropriate level of model complexity as shown in Fig. 1. The parameter uncertainty can be reduced by a calibration process, decreasing the resulting

Nomenclature

A	Pre-exponential factor [s^{-1}]
c	Specific heat [$\text{J}/(\text{kg K})$]
E_a	Activation energy [kJ/mol]
k	Thermal conductivity [$\text{W}/(\text{m K})$]
\dot{m}''	Mass loss rate [$\text{g}/(\text{s m}^2)$]
M	Model
n	Order of reaction $[-]$
N	Number of experimental points
T	Temperature [K]

Subscripts

∞	Ambient conditions
exp	Experiment
i	Model number

m	Mass loss rate
ref	Reference $T_{\text{ref}} = 300 \text{ K}$
S	At the surface
sim	Simulation
T_s	Surface temperature

Greek symbols

γ	Power properties evolution $[-]$
Δ	Prediction error
ε	Absorptivity/emissivity $[-]$
κ	Attenuation coefficient [m^{-1}]
ν	Yield of reaction $[-]$
ρ	Density [kg/m^3]
φ	Material properties
ϕ	Measurements

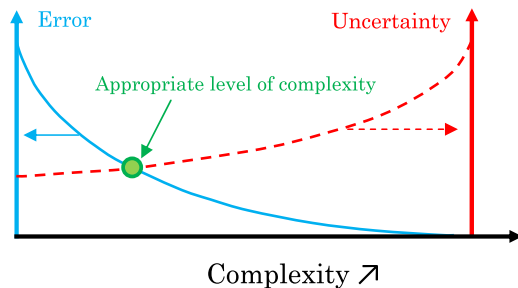


Fig. 1. Schematic of the relationship between prediction error, prediction uncertainty and model complexity.

prediction uncertainty. The appropriate level of complexity is therefore moving in the direction of growing complexity.

As the number of possible mechanisms grows the issue of how to determine the most beneficial level of model complexity becomes a major concern. This issue is of interest as well in the modeling of other phenomena outside fire science, for example see [6–8].

This paper explores the relationship between complexity and prediction error in the pyrolysis modelling of a non-charring material. This phenomenon is one of the most important and best known problems in fire science. Moreover, it is fundamental in the context of solid ignition and fire growth.

The predictions from a range of pyrolysis models are compared in order to investigate their sensitivity to the heat, mass and chemical mechanisms. This approach diverges from previous sensitivity analyses found in the literature which focused on the parameter sensitivity [9,10]. Instead, this methodology studies the evolution of the predictions by adding one-by-one assumptions to a base model corresponding to the highest complexity (i.e. most complete set of pyrolysis mechanisms from a particular code [2]), until a relatively simple set of equations is reached.

2. Several model complexities for one set of experiments

2.1. Comparison to experiments

The prediction capability of a pyrolysis model is usually inferred from comparison against transient measurements of mass loss rate \dot{m}'' and surface temperature T_s . One of the most complete sets of pyrolysis measurements in the literature is that by Kashiwagi and Ohlemiller

[11]. They exposed vertical samples of clear PolyMethylMethAcrylate (PMMA), 15 mm thick, to two different radiative heat flux levels (17 and 40 kW/m^2) in several atmospheric compositions (from 0% to 40% in oxygen concentration) and provided measurements of \dot{m}'' and T_s . They have estimated their measurement uncertainty to be of 5% for \dot{m}'' and 3% for T_s .

These high quality experiments have been used for comparison to model predictions by Lautenberger and Fernandez-Pello [2], Kashani and Esfahani [12] and Staggs [13]. Part of the comparisons between these predictions and the measurements is shown in Fig. 2. Note that among the experiments considered, Staggs [13] predicts only one set of conditions (40 kW/m^2 and inert atmosphere) whereas Lautenberger and Fernandez-Pello [2] and Kashani and Esfahani [12] compared to all four sets.

The predictions of T_s extracted from the three papers are in good agreement with the experimental results for all conditions. While the predictions from Lautenberger and Fernandez-Pello [2] are almost always within the experimental uncertainty at 40 kW/m^2 for both atmospheric compositions, they slightly overestimate T_s at 17 kW/m^2 . Their predictions are overall the best, but Kashani and Esfahani [12] obtain better results at 17 kW/m^2 in 20% oxygen.

From a general point of view, the predictions of \dot{m}'' in the three papers (Fig. 2), present greater discrepancies to the experiments than the temperature predictions. The errors are larger than the experimental uncertainty. Similarly to T_s , the predictions of Lautenberger and Fernandez-Pello [2] are the most accurate at 40 kW/m^2 , even if the numerical results do not capture correctly the early stages ($< 3 \text{ g}/(\text{m}^2 \text{ s})$) in the presence of oxygen (maximum error $\approx 1 \text{ g}/(\text{m}^2 \text{ s})$ at 60 s). At 17 kW/m^2 in the presence of oxygen, it is the predictions from Kashani and Esfahani [12] which estimate best \dot{m}'' . Overall, all three papers capture approximately the shape of \dot{m}'' but fail to predict the onset of pyrolysis.

Due to the relative similarity in their predictions, it is interesting to compare the mechanisms including the models extracted from these papers.

2.2. Differences in the model equations

The three papers use different codes to implement their models. This section focuses on the difference between the implemented equations. The three models solve the energy conservation equation in the solid, but the mass of the condensed phase is not always conserved (regression assumed negligible by Kashani and Esfahani [12]).

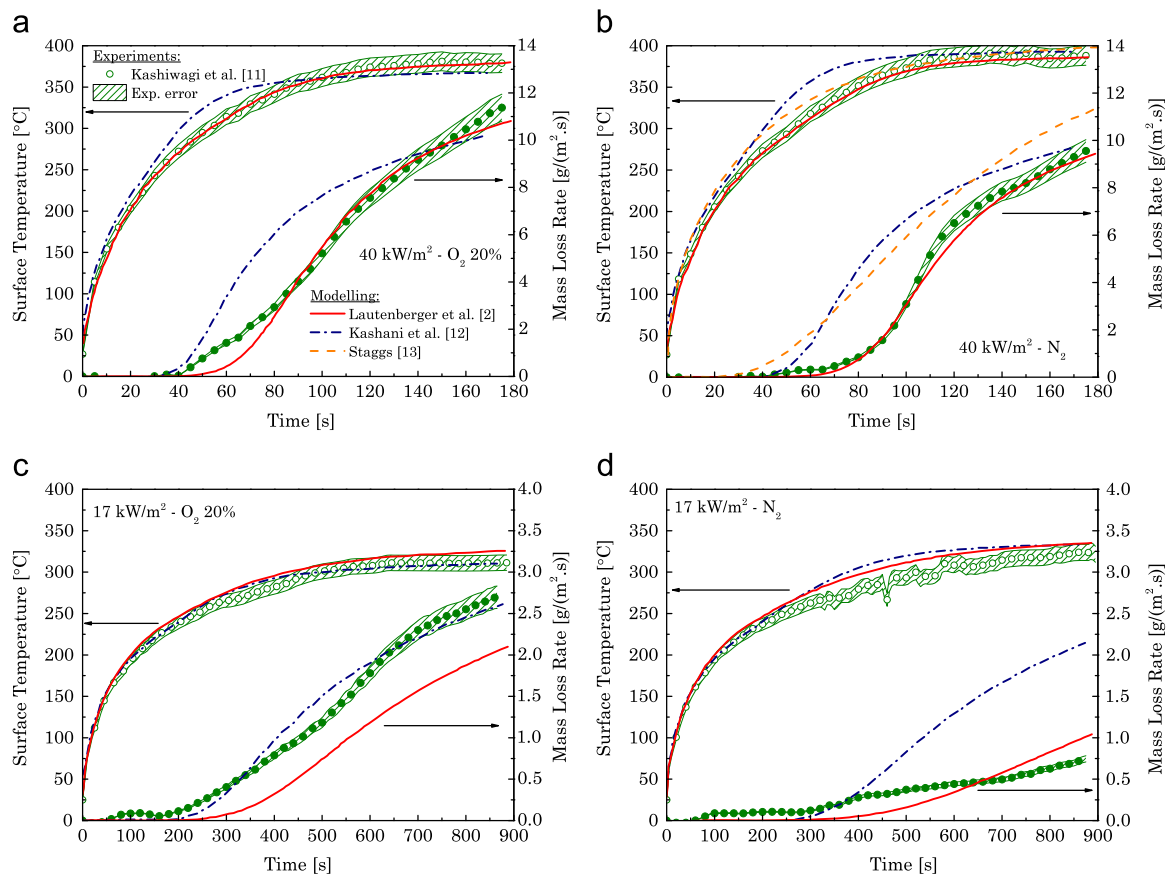


Fig. 2. Numerical predictions of surface temperature and mass loss rate from the literature against the experimental measurements for clear PMMA: (a) and (b) at 40 kW/m^2 ; (c) and (d) at 17 kW/m^2 ; (a)–(c) in 20% oxygen concentration and (b)–(d) in nitrogen atmosphere.

The gas phase treatment differs between the models. Staggs [13] does not consider any conservation equation in the gas phase. Lautenberger and Fernandez-Pello [2] solve the momentum equation for the gas transport across the solid matrix and assume thermal equilibrium between the condensed and gas phases. Kashani and Esfahani [12] solve the energy and species conservation equations for the gas but only above the front surface.

Although the three models base the quantification of \dot{m}'' on an Arrhenius kinetics law, the reaction schemes differ. Lautenberger and Fernandez-Pello [2] used a three-steps reaction scheme whereas Kashani and Esfahani [12] and Staggs [13] considered only one-step. Staggs [13] is the only one that does not include oxidative reaction. For Lautenberger and Fernandez-Pello [2] (only one step sensitive to oxygen) and Kashani and Esfahani [12], the Arrhenius term of the oxidative reaction includes a factor varying with the oxygen concentration.

Absorption of the incident radiative heat flux is also treated differently. Staggs [13] assumes that the radiation is only absorbed at the surface (as a boundary condition), whereas the two other models consider in-depth radiation absorption (Beer–Lambert's law). While Lautenberger and Fernandez-Pello [2] keep the attenuation coefficient constant and uniform, Kashani and Esfahani [12] use a transient attenuation coefficient to account for bubbles formation during in-depth degradation. Lautenberger and Fernandez-Pello [2] simulate the effect of bubbles by introducing an intermediate solid species with different material properties than the virgin PMMA (PMMA \rightarrow β PMMA—where β PMMA stands for bubbled PMMA).

Only Lautenberger and Fernandez-Pello [2] use thermal properties varying with temperature whereas the others assume constant and uniform properties.

Finally, the treatment of the convective heat losses varies also between models. Lautenberger and Fernandez-Pello [2] consider the convective heat transfer coefficient as constant at both boundaries, whereas Kashani and Esfahani [12] take it as function of T_s . Staggs [13] assumes a constant convective heat transfer coefficient at the front surface but the back boundary was adiabatic (heat losses negligible).

2.3. Parameter values

The three models have been calibrated differently. Staggs [13] used data extracted from the literature except for the determination of the kinetics couple (pre-exponential factor A and activation energy E_a) which was obtained from an independent thermogravimetric analyses (TGA). Kashani and Esfahani [12] used also mainly the data from the literature but the radiative properties (attenuation coefficient and reflectivity) and the oxygen sensitivity of the pyrolysis degradation were optimised based on the measurements from Kashiwagi and Ohlemiller [11]. Lautenberger and Fernandez-Pello [2] optimised most of their parameters by inverse modelling with the full set of measurements from Kashiwagi and Ohlemiller [11].

The values of the material properties used in the three papers differ significantly but they all fit inside the ranges of variability observed for PMMA in the literature [14]. In particular, the values for the kinetics couple fall inside the very wide range of variability shown in Fig. 3 (which reports 60 kinetics couples found in the literature for PMMA). The wide range of values and the linear relationship between them are indicative of the compensation effect. The techniques employed to extract these couples are emphasised in Fig. 3.

Hirata et al. [15], performed TGA on PMMA samples from the same supplier as in Kashiwagi and Ohlemiller [11]. They found that while a

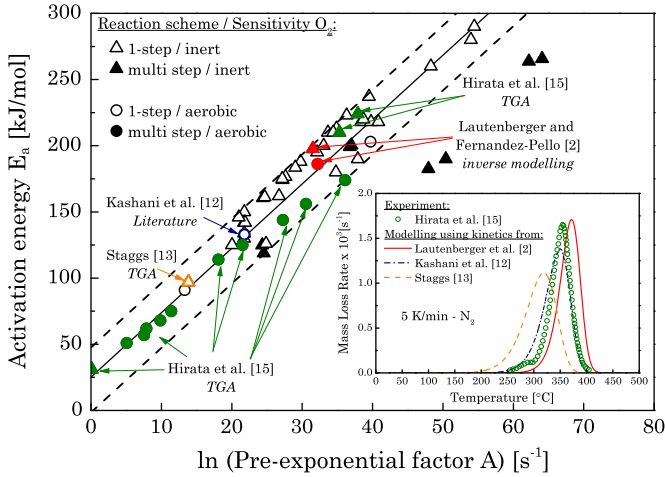


Fig. 3. Kinetics parameters for PMMA pyrolysis collected from the literature. Inset: comparison between experimental and numerical results of TGA at 5 K/min in inert atmosphere.

one-step reaction suffices to describe the chemical degradation in nitrogen atmosphere, three steps were required in air.

Using a one-step Arrhenius equation ($PMMA \rightarrow GAS$) with the kinetics couples reported by each of the three papers [2,12,13], the thermogravimetry is predicted in nitrogen at 5 K/min and compared in the inset of Fig. 3 to the experimental results by Hirata et al. [15]. Staggs' kinetics [13], obtained from independent TGA performed at 10 K/min, predicts the temperature for the peak mass loss within 10% of error. However, the magnitude of the peak mass loss is predicted within 32% of error. Lautenberger and Fernandez-Pello [2], who performed an inverse modelling using the experimental data (Fig. 2) from Kashiwagi and Ohlemiller [11], predict the temperature and the magnitude of the peak with less than 5% of error. This agreement is excellent considering the difference in the heating rate between the thermogravimetric prediction (5 K/min) and the small scale experiment from Kashiwagi and Ohlemiller [11] (estimated heating rate < 1 K/s [16]). The predictions using the kinetics from Kashani and Esfahani [12] (values that they have extracted from the literature) fall between the two others.

The discrepancy between the thermogravimetry simulations and the experimental results in air (not shown here) is significantly higher in the number of peaks, magnitude and location.

Even if the agreement between the pyrolysis is not consistent, the three models present similarities in the predictions whereas the included mechanisms and the values of the input parameters present large differences. This demonstrates that there is some degree of unnecessary complexity in the models and some non-relevant parameters that nonetheless add modelling uncertainty. It is therefore important to identify the mechanisms that control the modelling accuracy.

3. Mechanism sensitivity

3.1. Taxonomy of model complexity

In this section, the predictions of different models are compared to the experimental results from Kashiwagi and Ohlemiller [11] at 40 kW/m^2 (Fig. 2). The taxonomy of the models is obtained by adding, one-by-one, assumptions to the model used by Lautenberger and Fernandez-Pello [2] and called M_1 hereafter. It represents the highest level of complexity (i.e. most complete set of mechanisms). At each assumption or approximation, a new model M_{i+1} is obtained and used to predict T_S and \dot{m}'' with the same values for the input parameters as for M_1 . In this novel

approach based on a mechanism sensitivity, the values of the input parameters are assumed to correspond to the true material properties and are therefore kept unchanged in order to reveal the influence of the simplifications. The code used is GPYRO [2].

M_1 is based on mass, species and energy balances for the condensed phase. Source terms included in the energy conservation encompass the energy consumed by the chemical reactions and the in-depth radiation absorption. In addition, the mass, species and momentum conservation equations are solved for the pyrolysis gases inside the solid matrix. The momentum equation enables the consideration of the gas pressure evolution and the description of the mass flux of gases released at the front surface instead of assuming an instantaneous release of the pyrolysis gases produced in depth. The pyrolysis degradation is composed of a three-step reaction scheme (Eqs. (1)–(3)).



In the first reaction (Eq. (1)), the solid species PMMA produces another solid species called $\beta PMMA$. This reaction allows variations of the material properties to account for the formation of bubbles. This reaction does not absorb energy (i.e. heat of pyrolysis $\Delta H = 0 \text{ kJ/kg}$). The two other reactions produce pyrolysis gases: one by thermal degradation (Eq. (2)) whereas the other by oxidative degradation (Eq. (3)). They are both assumed endothermic. These reactions are modelled by the Arrhenius laws with the kinetics triplet: pre-exponential factor A , activation energy E_a and order of reaction n . The material properties (thermal conductivity k , specific heat c and density ρ), expressed generically by φ , are allowed to vary with temperature in Eq. (4) following a power law controlled by γ_φ . This temperature dependency implies swelling if $(T/T_{ref})^{\gamma_\rho} > 1$, or shrinking if $(T/T_{ref})^{\gamma_\rho} < 1$ due to thermal effects prior to any reaction.

$$\varphi = \varphi_\infty \left(\frac{T}{T_{ref}} \right)^{\gamma_\varphi} \quad \varphi \in \{k; \rho; c\} \quad (4)$$

The radiation absorption (non-reflected fraction of the incident radiation based on the absorptivity/emissivity ϵ) is assumed to occur in depth using Beer–Lambert's law with a finite attenuation coefficient κ . The full set of equations is detailed elsewhere [2].

From this model, a set of assumptions is added to gradually decrease its complexity. Table 1 gathers the different assumptions referenced by letters from A to I. These can be classified in three groups: (1) mass transfer {A}, (2) chemical degradation {B, C, E, G} and (3) heat transfer {D, F, H, I}.

The order in which each assumption is invoked is not unique. The impact of this order could be important and so an alternative order is also investigated in this study. A total of 17 models have been created. An *a priori* order, illustrated in Fig. 4, has been investigated first. It specifies the taxonomy α which reflects the overall ranking of complexity typically found in the literature. Some examples follow. Stoliarov et al. [9] used a model similar to M_4 . The small difference resides in the mathematical formulation of some mechanisms such as for in-depth absorption. Bal and Rein [17] predicted the delay time to ignition at high heat fluxes with a model equivalent to M_6 . Cordova and Fernandez-Pello [18] used a model equivalent to M_7 to predict as well the delay time to ignition. Their model differs slightly from M_7 since Cordova and Fernandez-Pello [18] included the endothermicity of the pyrolysis reaction (i.e. assumption D not invoked in their model). Jiang et al. [19] solved analytically a set of equations similar to those of M_8 . The difference being that Jiang et al. [19] assumed linear heat losses at the front surface (combination of convective and radiative heat losses). Finally, the classical ignition theory [20] corresponds

Table 1
Assumptions and simplifications added to model M_1 .

Letter	Assumption	Group	Definition and implementation
A	Gases released instantaneously	(1)	The produced gases are released without resistance (low viscosity). Gas phase momentum equation is not solved.
B	Oxidation negligible	(2)	The solid decomposition is anaerobic. The reaction in Eq. (3) is removed.
C	One-step chemical reaction	(2)	The chemical degradation is described with only one reaction. Eqs. (1) and (2) are replaced by $\text{PMMA} \rightarrow \text{GAS}$.
D	Heat of pyrolysis negligible	(3)	The energy consumed (or produced) by a chemical reaction is negligible. Heat of pyrolysis sets to 0 kJ/kg.
E	Solid phase consumption negligible	(2)	The mass lost by the solid is negligible. The one-step reaction is replaced by $\text{PMMA} \rightarrow \text{PMMA}$.
F	Thermo-physical properties invariant	(3)	The material properties are considered independent of temperature. γ_ϕ from Eq. (4) sets to 0.
G	Inert solid	(2)	The chemistry degradation process is negligible. The chemical reaction is removed.
H	In-depth absorption negligible	(3)	The incident radiative heat flux is absorbed at the surface. Attenuation coefficient sets to infinity.
I	Reflectivity negligible	(3)	All the incident heat flux is absorbed by sample. Absorptivity/emissivity equal to unity.

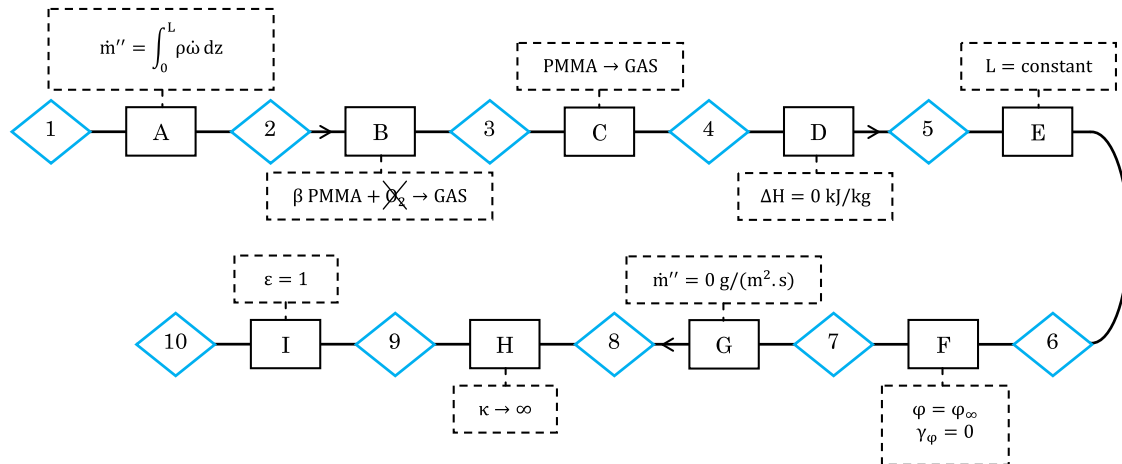


Fig. 4. Model taxonomy α (diamond: models and square: assumptions).

to an analytical solution of M_{10} but without the heat losses at the boundary.

3.2. Results and discussion

The error between the experimental and numerical results, called Δ hereafter, is defined in Eq. (5). The experimental data set used is that of Kashiwagi and Ohlemiller [11] at 40 kW/m² (see Fig. 2a and b).

$$\Delta = 1 - \left(\frac{1}{N} \sum \left(\frac{\phi_{\text{exp}}}{\text{diff}(\phi_{\text{exp}} - \phi_{\text{sim}}) + 0.05 \phi_{\text{exp}}} \right)^2 \right) / \left(\frac{1}{0.05} \right)^2 \quad [\%] \quad (5)$$

$$\text{diff}(\phi_{\text{exp}} - \phi_{\text{sim}}) = \begin{cases} |\phi_{\text{exp}} - \phi_{\text{sim}}| & \text{if } \phi_{\text{sim}} \notin \text{in experimental error} \\ 0 & \text{if } \phi_{\text{sim}} \in \text{in experimental error} \end{cases}$$

where ϕ is the quantity of interest and N is the number of data points considered.

Two errors are considered: Δ_m associated with \dot{m}'' and Δ_{T_s} associated with T_s .

3.2.1. Taxonomy α

The models from the taxonomy α are used to predict \dot{m}'' and T_s at 40 kW/m² in 20% oxygen, keeping the values of the input parameters suggested by Lautenberger and Fernandez-Pello [2]. The predictions of the different models are plotted in Fig. 5.

The predictions of T_s with the models M_1 – M_4 show a good agreement with the experimental results since they are within the experimental uncertainty (not entirely for M_4). For M_5 and simpler models ($M_{i>5}$), T_s is overestimated. Cordova et al. [21] reported

similar results with their model close to M_{10} . They claimed that this overestimation was due to the assumption of negligible endothermic pyrolysis losses (assumption D, M_4 and M_5). However, Fig. 5 shows that assumption D leads to overestimations in T_s only after a certain threshold (≈ 325 °C).

The heat transfer assumptions, F (thermo-physical properties invariant, M_6 and M_7) and H (in-depth absorption negligible, M_8 and M_9) are also highly influencing (Fig. 5a) since both increase significantly the T_s overestimation.

Concerning the predictions of \dot{m}'' , the assumption of instantaneous release of the produced pyrolysis gases (assumption A, M_1 and M_2) seems not to affect the prediction.

The assumption of negligible oxidative reaction (assumption B, M_2 and M_3 –Eq. (3)) affects significantly the magnitude of \dot{m}'' but not its shape. Simplifying the reaction scheme to only one step, where PMMA produces directly gases (assumption C, M_3 and M_4), provokes significant changes in \dot{m}'' (mainly the magnitude) only after 4 g/(s m²) whereas neglecting the endothermicity (assumption D, M_4 and M_5) influences considerably its shape. Note that for the prediction of ignition using a critical mass flux criterion, the results in Fig. 5b show that the endothermicity has a negligible effect (at least at 40 kW/m²) since the ignition criterion is generally considered ≤ 3 g/(m² s) and the predictions from M_4 and M_5 are close up to this threshold. \dot{m}'' is not calculated for model M_i , where $i > 7$ since assumption G sets the solid as inert.

The error Δ has been assessed using Eq. (5) in order to quantify the evolution of the predictions as a function of the model complexity (Fig. 6). The complexity has been quantified in two different manners: first as the total number of parameters in each model and second as the decreasing order of each model in the taxonomy.

The relationship between model complexity and Δ is monotonic but the shape varies greatly according to the quantity of

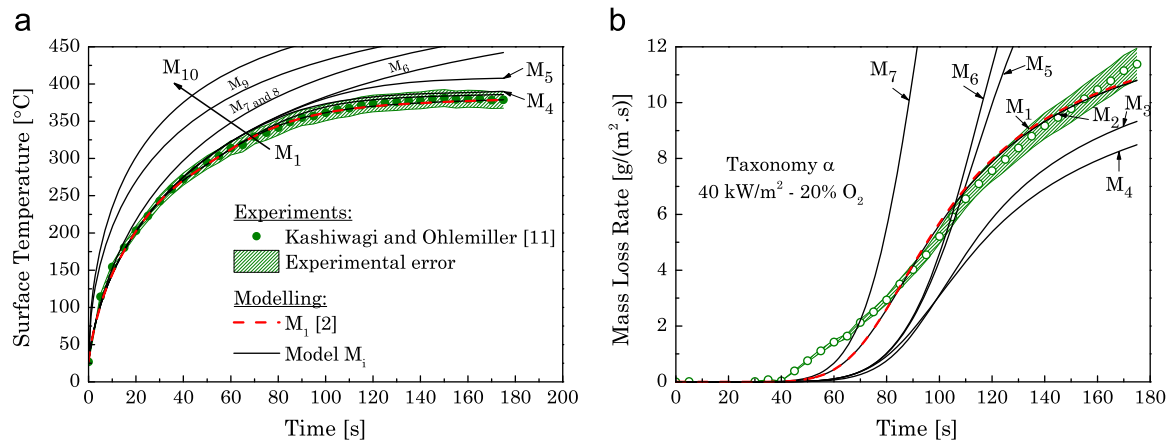


Fig. 5. Numerical predictions against experimental measurements at 40 kW/m² in 20% oxygen for models in taxonomy α : (a) surface temperature and (b) mass loss rate.

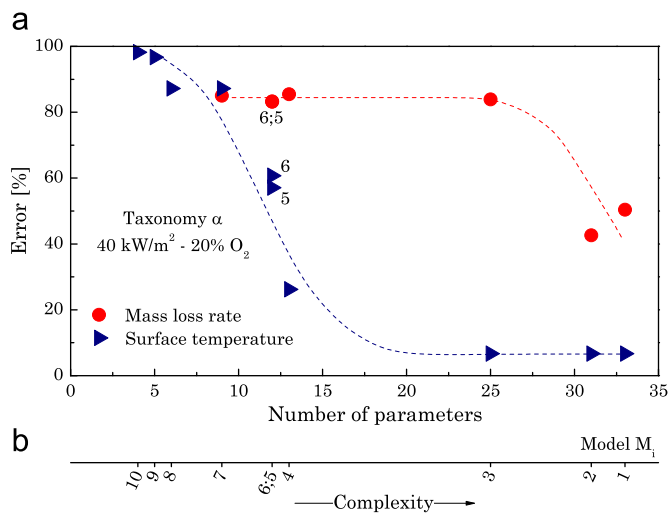


Fig. 6. Relationship between model complexity (taxonomy α) and prediction error for surface temperature and mass loss rate at 40 kW/m² in 20% oxygen. The x-axis represents (a) the number of parameters in the models and (b) the reference number of the models in the taxonomy.

interest: \dot{m}'' or T_s . ΔT_s ranges from 7% to 98% between M_1 and M_{10} whereas Δ_m ranges from 45% to 85% between M_1 and M_7 .

The complexity-error relationship for T_s presents a plateau at around 7% for high complexity (beginning of the taxonomy—high number of parameters) and suddenly increases below 25 parameters. This is where the assumption C (one-step chemical reaction, M_3 and M_4) is made, which alone increases the error by 20%. This significant increase in the quantitative result of the prediction error, not visible in Fig. 5a (qualitative result of the prediction error), comes from a small number of time-intervals where the predictions fall outside the uncertainty range of the measurements. A large impact on the complexity-error relationship for T_s is caused by assumption D (heat of pyrolysis negligible, M_4 and M_5). The assumption of negligible regression (assumption E, M_5 and M_6) does not affect the value of ΔT_s , but it affects the shape of T_s as shown in Fig. 5a. The temperature presents smoother curvature after 375 °C when the surface regression is considered.

While assumption F (thermo-physical properties invariant, M_6 and M_7) and assumption H (in-depth absorption negligible, M_8 and M_9) provoke similar qualitative effect as seen on Fig. 5a, only the former induces a significant jump in ΔT_s . Assumption H does not seem to have an impact because the error with M_8 is already overly large.

T_s is therefore predicted with reasonable accuracy (26% error) with only one-step reaction including losses by endothermicity,

thermal dependency of the material properties and in-depth radiation absorption. In this taxonomy, simpler models would result in an error of at least of 57%. Note that M_4 requires only 13 parameters instead of the 33 parameters for M_1 , reducing therefore significantly the calibration effort.

The relationship between Δ_m and model complexity shows the same monotonic shape but the sudden jump is at the opposite end of the complexity range. The predictions of \dot{m}'' diverge drastically from the experimental measurements as soon as a single simplification is made on the chemical degradation complexity. Δ_m goes from 43% to 84% when the oxygen sensitivity is neglected (assumption B, M_2 and M_3).

After only a few assumptions, Δ_m reaches a plateau at around 84%. At the opposite of the plateau observed for ΔT_s which is the consequence of no improvements when the complexity is increased, in the case of Δ_m , the plateau results from a large disagreement with the measurements. Even if assumptions C–F (added between M_3 and M_7) lead to significant changes in the predictions of \dot{m}'' (i.e. qualitative effect), the agreement between the prediction and the measurement is already poor with M_3 (Fig. 5b) and further simplifications do not influence much Δ_m (i.e. quantitative effect). The error does not increase above 84% because in the early stages (< 40 s), the experimental and predicted \dot{m}'' are both null. This small agreement corresponds therefore to the prediction of the time of the onset of pyrolysis.

It is worth mentioning that assumption A (gases released instantaneously, M_1 and M_2) improves the predictions (43% error with M_2 instead of 50% with M_1). While the physical phenomenon of mass transfer across the solid matrix has been observed experimentally, its mathematical formulation or calibration, as it is in M_1 , is not satisfactory. This would be a trivial case of unjustified complexity.

The TGA performed by Hirata et al. [15] reveals a large complexity of the reaction scheme in oxygenated atmosphere (three steps) whereas it seems to be composed only of one reaction in nitrogen (shown in inset in Fig. 3). By performing an equivalent analysis in nitrogen with the models from the taxonomy α , the high sensitivity of \dot{m}'' to the oxidation reaction is avoided and it is possible to assess the influence of the following assumptions ($M_{i>2}$). The models predictions for an inert atmosphere are plotted in Fig. 7.

For T_s , the evolution of the predictions with model complexity provides similar results as in 20% oxygen (Fig. 5). Only models simpler than M_4 (i.e. $M_{i>4}$) predict T_s outside of the experimental uncertainty. Independently of the chemistry assumed, the predictions of the surface temperature have a similar level of accuracy.

As expected, \dot{m}'' is not influenced by assumption B (oxidation negligible, M_2 and M_3) due to the inert atmosphere. The simplification of the reaction scheme with assumption C (one-step chemical reaction, M_3 and M_4), which removes the intermediate

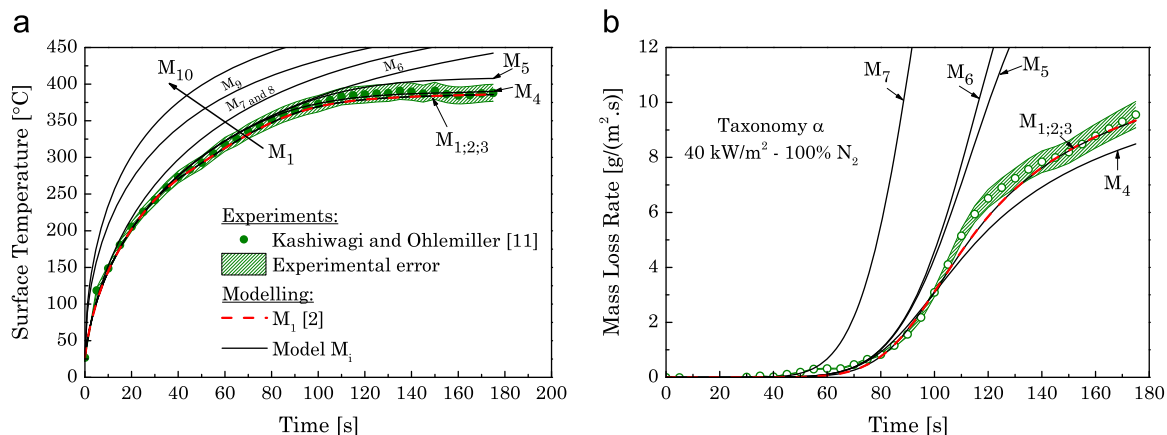


Fig. 7. Predictions against experimental measurements at 40 kW/m^2 in nitrogen for models in taxonomy α : (a) surface temperature and (b) mass loss rate.

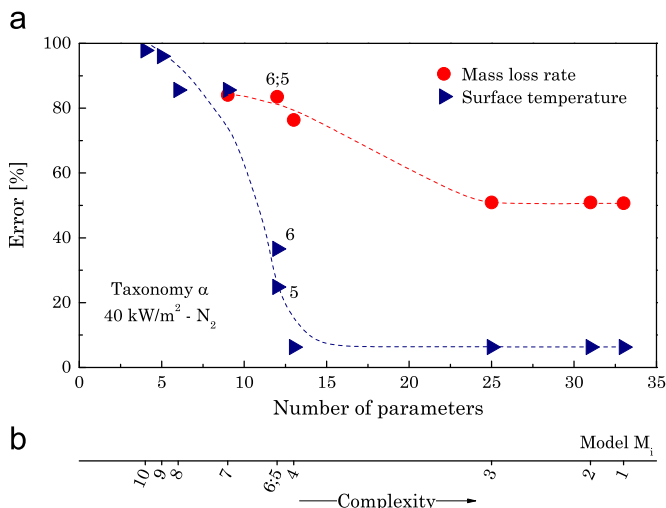


Fig. 8. Relationship between model complexity (taxonomy α) and prediction error for surface temperature and mass loss rate at 40 kW/m^2 in nitrogen. The x-axis represents (a) the number of parameters in the models and (b) the reference number of the models in the taxonomy.

species βPMMA , affects significantly the prediction of \dot{m}'' after $4 \text{ g}/(\text{m}^2 \text{ s})$. However, the shape of the predicted \dot{m}'' evolves with time in a similar manner than the experimental measurement until the endothermicity of the reactions is neglected (assumption D, M_4 and M_5). Then the shape of the predicted \dot{m}'' is drastically changed.

The quantification of the complexity-error relationship for the taxonomy α in inert atmosphere is plotted in Fig. 8. As it was observed in Fig. 7a, prediction of T_s is relatively well accurate up to M_4 . The overestimation resulting from M_5 appears only above 400°C , which corresponds to a higher temperature threshold than in oxygenated atmosphere. As a consequence, ΔT_s is only of 25% for M_5 , which is equivalent to the level of error reached with M_4 in oxygenated atmosphere. This decrease in required complexity (only 12 parameters in M_5) shows that the experimental conditions affect the mechanisms sensitivity. Indeed, the reduction of the predicted \dot{m}'' , caused by the absence of oxidative reaction (Eq. (3)), leads a lower level of heat losses by endothermicity and therefore a lower influence of the assumption D (heat of pyrolysis negligible, M_4 and M_5).

Assumption F (thermo-physical properties invariant, M_6 and M_7) increases ΔT_s to a similar level ($\approx 87\%$) of that in oxygenated atmosphere for the same number of parameters.

The prediction of \dot{m}'' appears again to be significantly sensitive to a change of the reaction scheme. Δ_m increases from 51% to 84% with the simplification of the reaction scheme to only one-step (assumption C,

M_3 and M_4). Eq. (1) is not the rate-limiting step in models $M_i < 4$, meaning that the pyrolysis reaction producing the gas (Eq. (2)) is not regulated by the production of solid species βPMMA . The suppression of this species by assumption C induces therefore changes only on the material properties. The production rate of gases, being dependent of the density and the local temperature (which depends on the thermo-physical properties k , ρ and c , so on the heat transfer mechanisms) is therefore affected.

While the predicted shape of \dot{m}'' with M_4 appears close to the experimental measurements, as seen in Fig. 7b, the quantification of Δ_m indicates that the predictions are only slightly better than those using M_5 .

As a conclusion of the investigations performed on taxonomy α , the mechanisms controlling the prediction of \dot{m}'' and T_s seem different. In the case of \dot{m}'' , the prediction accuracy is significantly decreased as soon as an assumption is made on the chemical mechanisms. While in air the experimental results show that the chemical decomposition is relatively complex, in nitrogen, the degradation is well described with only one-step. A detailed analysis of the predictions in inert atmosphere shows that \dot{m}'' is affected also by the evolution of the temperature (mechanisms of heat transfer).

In the case of T_s , accurate predictions can be achieved with a relatively low complexity: only 12 or 13 parameters (depending of the atmosphere) instead of 33 with M_1 . The mechanisms affecting mostly the results are related to heat transfer (i.e. group (1) from Table 1: heat of pyrolysis negligible-assumption D, thermo-physical properties invariant-assumption F and in-depth absorption negligible-assumption H).

The taxonomy α reveals that \dot{m}'' requires a high level of complexity concerning the chemical mechanisms, whereas T_s does not. Some results indicate that heat transfer can also affect \dot{m}'' . The particular order of the assumptions in taxonomy α does not allow for a complete investigation of the sensitivity of \dot{m}'' to the heat transfer mechanisms. For this reason, a second taxonomy, called β and presented in Fig. 9, is investigated.

3.2.2. Taxonomy β

Taxonomy β is such that the assumptions related to the heat transfer are made before simplifying the chemical degradation complexity. This taxonomy is applied at 40 kW/m^2 in 20% oxygen. The predictions for T_s and \dot{m}'' are shown in Fig. 10.

As in taxonomy α , neglecting the endothermic heat losses (assumption D, M_2 – M_{11}) provokes the prediction of T_s to fall outside the experimental uncertainty after a certain temperature threshold (around 375°C for taxonomy β in 20% oxygen). However, in opposition to taxonomy α , in taxonomy β the complete reaction scheme (Eqs. (1)–(3)) is still considered when assumption D is

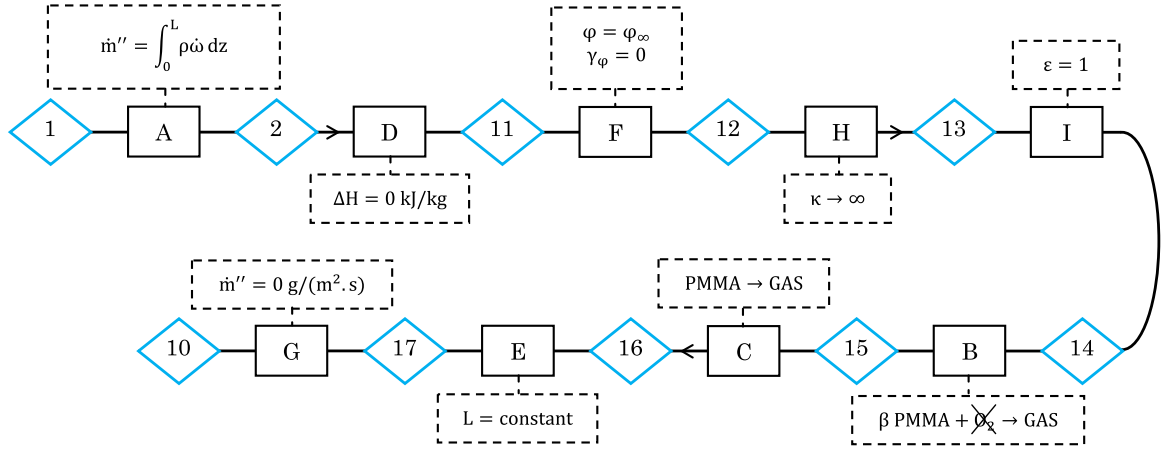


Fig. 9. Model taxonomy β (diamond: models and square: assumptions).

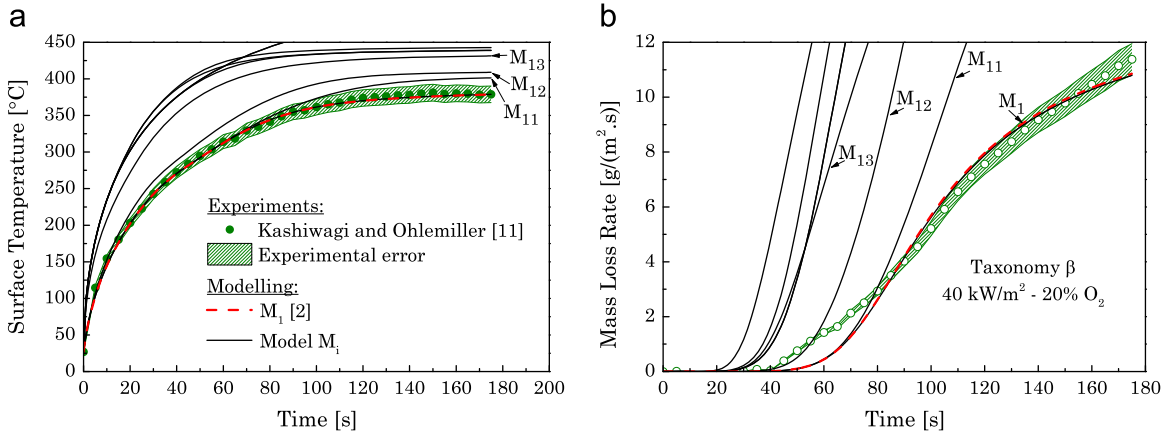


Fig. 10. Predictions against experimental measurements at 40 kW/m² in 20% oxygen for models in taxonomy β : (a) surface temperature and (b) mass loss rate.

made. This confirms that the increase of error in the prediction of T_s is not related to assumptions on the chemistry (from three-step to only one-step). This is of great importance since it makes possible to calibrate the heat losses by endothermicity without predicting the exact reaction rates but by using the measured mass loss rate.

The prediction of T_s falls mainly out of the experimental uncertainty once the material thermal dependency is neglected (assumption F, M_{11} and M_{12}). However, the predictions using M_{12} stays close to the experimental measurements and the largest effect on the transient evolution of T_s is obtained by the simplification of the radiation absorption mechanism (assumption H, M_{12} and M_{13}).

The predictions of \dot{m}'' (Fig. 10b) are also significantly influenced by heat transfer simplifications: endothermic heat losses negligible (assumption D, M_2 – M_{11}), invariant material properties (assumption F, M_{11} and M_{12}) and radiation absorption at the surface (assumption H, M_{12} and M_{13}).

The complexity-error relationship Δ for T_s and \dot{m}'' , resulting from the taxonomy β , is plotted in Fig. 11. The two curves have a similar shape for both quantities demonstrating that they are affected by the same simplifications.

As it is observed in Fig. 11, with only three assumptions (endothermic heat losses negligible, invariant material properties and absorption of the external radiation at the surface, respectively D, F and H, M_2 – M_{13}), Δ_{T_s} increases from 7% to 95%. This influence of the heat transfer mechanisms on Δ_{T_s} is in agreement with the result seen for taxonomy α . Δ_{T_s} is more sensitive to assumption F (thermo-physical properties invariant, M_{11} and M_{12}) than assumption H (in-depth absorption negligible, M_{12} and M_{13}) whereas the transient prediction in Fig. 10a shows the opposite influence.

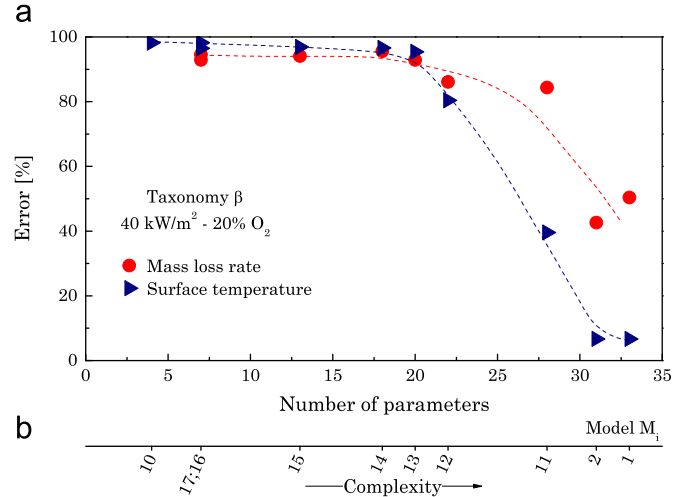


Fig. 11. Relationship between model complexity (taxonomy β) and prediction error for surface temperature and mass loss rate at 40 kW/m² in 20% oxygen. The x-axis represents (a) the number of parameters in the models and (b) the reference number of the models in the taxonomy.

The quantification of Δ_m confirms that the heat transfer mechanisms have also a large influence on \dot{m}'' . The plateau reached by Δ_m in this taxonomy is higher (95%) than in taxonomy α (84%) because the models predict a shorter pyrolysis time (onset of decomposition) in this taxonomy (Fig. 10b).

The prediction capability of a pyrolysis model is therefore intimately linked to the accuracy of the energy distribution inside the solid sample. Considering the importance of heat transfer, in-depth temperature measurements are essential to validate the correct implementation of these mechanisms. Unfortunately, in-depth temperature measurements are rare in the literature.

In our taxonomies, the material properties are either all function of temperature (Eq. (4)) or all constant. However, it might that some need to be taken constant and others not. For example, the thermal conductivity varies little between 20 °C and 300 °C ([0.16; 0.20] W/(m K) numerically [2], and [0.14; 0.22] W/(m K) experimentally [14]). Further sensitivity analyses could be performed including both temperature and mass loss measurements (since ρ is present in both the heat equation and the reaction rate [2]).

4. Conclusion

While one of the first modelling tasks is to select the appropriate conceptual model to simulate a physical phenomenon, detailed justifications of the inclusion or exclusion of the different mechanisms are infrequent and the model complexity is often subjective. A brief comparison of three models (implemented in different codes) used for predicting the same experimental results reveals that some degree of complexity in their mechanisms is unnecessary.

A novel approach corresponding to a mechanism sensitivity (parameters kept constant) is used to identify the predominant mechanisms for transient pyrolysis. From one of the most complex pyrolysis models for a non-charring polymer available in the literature, a series of assumptions and simplifications have been made; reducing step-by-step its complexity. The specific order of these assumptions defined a particular taxonomy of model complexity and the influence of this order is investigated as well via two taxonomies (17 different models in total).

The capability of these models to predict the pyrolysis behaviour of clear PMMA has been observed from the transient evolution of the mass loss rate and the surface temperature at 40 kW/m² in two different atmospheric compositions. The qualitative and quantitative evaluations of the disagreement between experimental and numerical results show an increase of the prediction error when model complexity is decreased. While the error increase is expected in general terms, the shape of the complexity-error relationship is unknown *a priori*. This study shows that the relationship is strongly dependent of the observed quantity of interested.

The mechanisms of heat transfer are the most important and their simplifications provoke a large increase of the error in the predictions for the surface temperature whatever complexity is considered for the chemical mechanisms. In the case of simple chemistry (one-step reaction), neglecting the endothermic heat losses, the thermal dependency of the material properties and the mechanism of in-depth absorption implied in this study an increase from 25% to 96% for the error of the surface temperature predictions (taxonomy α). If more complex chemistry is considered (three-steps reaction), the same heat transfer simplifications lead to an increase from 7% to 96% in error for the surface temperature (taxonomy β). Moreover, in the latter case, the prediction of the mass loss rate is also significantly affected by the heat transfer simplifications (error from 43% to 83%).

The complexity associated with the mass transfer (i.e. gas pressure evolution) appears to be negligible in this study.

The transient predictions of the mass loss rate \dot{m}'' are significantly affected by the level of complexity of the chemical mechanisms. However, according to this study, without a good prediction of the energy distribution and the heat losses (i.e. heat transfer process), the prediction of \dot{m}'' could not be accurate neither. It is therefore recommended to use consistent levels of crudeness dictated by the heat transfer and not to include large chemical complexity if the heat transfer is kept simple.

Like a parametric sensitivity study, the results are specific to the cases studied (i.e. experimental conditions). More investigations are required varying experimental conditions, materials and taxonomies. A global optimisation of the required mechanisms might be assessed using sophisticated techniques such as genetic algorithms applied on the selection of the mechanisms.

Acknowledgements

The authors would like to thank BRE Global, UK, and FM Global, USA, for their financial support to this research.

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